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Use of Acids and Acidulants on Alkali Soils and Water

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I. INTRODUCTION

The use of acidulants on irrigated soils of the western USA dates back to the 1930s. Prior to that time, gypsum was considered the amendment for sodium-affected soils. Hilgard (1889), for example, noted that "in the case of black alkali, the impenetrability of the surface soil itself renders underdrains ineffective, unless sodium carbonate, with its compacting effects on the soil, is first destroyed by the use of gypsum." By the mid 1930s, the use of sulfur was proposed along with the understanding of microbial oxidation to H_2SO_4, and subsequent dissolution of $CaCO_3$ and removal of exchangeable Na by Ca (Kelley and Brown, 1934; McGeorge and Green, 1935). When the USDA *Handbook 60* was published in 1954, a number of inorganic chemicals, including acids and acidulants, were cited as being potentially effective amendments (USSL Staff, 1954). However, the experimental data to substantiate these possibilities were limited. The first extensive field evaluation of sulfuric acid, along with sulfur and gypsum as an amendment for sodic alkali soils, was conducted in 1951 in the Central Valley of California with some impressive results (Overstreet et al., 1951). Starting in the late 1960s, pollution abatement activities at various industries intensified, and sulfuric acid became readily available from SO_2 scrubbing from smelter gases in the southwestern states (McKee, 1969). Sulfur recovery from natural gas and oil refining has also increased, and so has research to utilize these products on sodic or alkali soils and water (e.g., Miyamoto et al., 1975a).

Today, sulfuric acid and elemental S are used singly or in combination with various nitrogen compounds for improving sodic or alkali soils and irrigation

water. These uses may be categorized into two types: conditioning of alkali or sodic irrigation water, mainly to control Ca precipitation and/or to maintain soil structure and water infiltration; and treatment of sodic calcareous or sodic alkali soils, mainly to lower soil sodicity, pH, and/or to improve water infiltration, and at times, availability of certain micronutrients. The areas where these types of treatments are potentially beneficial are large worldwide (e.g., Dudal and Purnell, 1986; Bower and Fireman, 1957), and the applications range from intensive irrigated crop production to revegetation of sodium-affected lands. However, treatment effects are highly soil and site specific. The purpose of this chapter is to outline the conceptual basis for using acids and acidulants on sodic or alkali soils and water, and to provide some guidelines for their usage.

II. SOURCES AND PROPERTIES OF ACIDS AND ACIDULANTS

A. Acids

1. Sulfuric Acid

The sources of sulfuric acid include the acid produced from the oxidation of elemental S, by-product acids from smelting and wet scrubbing of SO_2, spent sulfuric acid from the gasoline alkylation process (Weiss et al., 1953), and waste sulfuric acid from various industrial processes (Tisdale, 1968; Beaton and Fox, 1971). The concentration of sulfuric acid varies with the source, but sulfur-burn acid and smelter acid are usually marketed at ingredient concentrations of 93 to 95%. Sulfuric acid with a concentration exceeding 98% readily freezes at low temperatures and generates hazardous SO_2 fumes at room or elevated temperatures. All types of sulfuric acid are highly corrosive, and its handling must be carried out in accordance with applicable safety, transportation, storage, and handling regulations, which are becoming stringent. Some of the properties of sulfuric acid are shown in Table 1.

2. Phosphoric Acid

The main source of phosphoric acid is from sulfuric acid digestion of phosphorus containing rocks, such as apatites or fluorapatites (Phillips and Webb, 1971). A by-product, gypsum ($CaSO_4 \cdot 2H_2O$) is separated out from phosphoric acid, while another by-product, HF, is usually recovered as sodium fluorosilicate. The concentrations of phosphoric acid from the wet digestion process are usually low but are elevated to 55 to 75% (17 to 24% P) prior to shipment. Superphosphoric acid produced through a special process contains higher concentrations, but the resulting high viscosity can present handling difficulties. Phosphoric acid is also corrosive and must be handled in accordance with applicable safety and handling regulations.

Table 1 Properties of Acids and Acidulants Used for Conditioning or Treating Alkali Soils and Irrigation Water

Materials	Formula	Molecular wt.	Ingredient % wt	Density kg L^{-1}	Ca release mol/mol
Acids					
Sulfuric acid	H_2SO_4	98	93–95	1.82–1.83	1.0
Phosphoric acid	H_3PO_4	98	55–75	1.45–1.6	1.5
Urea-sulfuric acid	$CO(NH_2)_2\ H_2SO_4$	60 + 98	94–95	1.50–1.55	1.0[a]
Ammonia-sulfuric acid	$(NH_4)_x{\cdot}H_2SO_4$	$(18)_{1.0}$ + 98	—	—	1.0[a]
Acidulants					
Elemental sulfur	S	32	99	2.0	1.0
Ammonium polysulfide	NH_4S_x[a]	18 + $(32)_{1.0}$	94	1.17	2.0
Iron sulfate	$FeSO_4{\cdot}7H_20$	278	98	1.89	1.0
Aluminum sulfate	$Al_2(SO_4)_3{\cdot}18H_20$	666	98	1.69	3.0
Acidic gases					
Sulfur dioxide	SO_2	64	99	1.43	1.0
Carbon dioxide	CO_2	44	99	1.10	1.0

[a]Assumed to be 1:1 molar mixture, and the contribution of N compounds on Ca release is included.

3. Acid Blends

Urea, $(NH_2)_2CO$, a polar compound, is soluble in sulfuric acid and is easily blended to form urea-sulfuric acid solutions. The reaction is endothermic, and it lowers the corrosiveness of sulfuric acid somewhat. The blending ratio varies, but a typical blend consists of one mole of urea against one mole of acid, which provides a product 17-0-0-19(S). This product was originally used for alleviating drip emitter clogging but is now used as a water conditioning chemical and a liquid acid-N fertilizer in sodic or alkali soils.

Urea is also added to phosphoric acid to form a solid granule compound, 17.5-44.4-0. This is a form of N-P fertilizer and has the advantage of easier handling than phosphoric acid, yet it retains the characteristics of acidic compounds when applied to either water or soils (Achorn, 1984).

Another form of acid application is a simultaneous injection of sulfuric acid and ammonia gas (NH_3) into irrigation water flow. The simultaneous injection idea was originally proposed to reduce NH_3 volatilization and Ca precipitation induced by water application of NH_3 or NH_4OH (Miyamoto and Ryan, 1976). Premixing of NH_3 and H_2SO_4 results in violent reactions and precipitation of $(NH_4)_2SO_4$. Thus the two compounds are applied to irrigation water separately. The application ratio is usually one mole of acid against two moles of NH_3 plus additional acid to remove approximately 90% of the bicarbonate concentration of irrigation water. This provides for complete neutralization of NH_3 (or NH_4OH) and the necessary conversion of HCO_3^- and CO_3^{-2} to H_2CO_3.

4. Other Acids

Theoretically, both nitric and hydrochloric acids can also be used for alkali soil and water treatments. However, these acids are rarely used, for various reasons including high costs, volatility, and handling difficulties. High dosages of HCl can also pose potential Cl toxicity to some crops, and excessive applications of HNO_3 can cause ground water contamination with NO_3^-.

B. Acidulants

1. Elemental Sulfur

Elemental sulfur (S) is among the oldest soil acidifying compounds used commercially. Sources include natural deposits of brimstone, sulfur recovered from natural gas containing H_2S, and petroleum desulfication (Beaton and Fox, 1971). Some sulfur is produced through the reduction of SO_2 waste gases and sulfate salts. Elemental sulfur is marketed in a wide array of forms, ranging from flakes, aggregates, and powders to suspended slurry (Tisdale, 1968). Sulfur dust is an irritant to eyes and subject to fire hazards. The purity of elemental sulfur was rather variable, but today has improved to 99% plus. Solid forms of elemental sulfur are stable in storage and provide high acidification poten-

tial per unit weight. Iron pyrite (FeS) is another source of S and is discussed in a separate chapter (Chapter 9).

2. Polysulfides of Ammonium or Calcium

Ammonium polysulfide, NH_4S_x, is manufactured by reacting sour gas (H_2S) with aqueous ammonia. The ratios of NH_3 and S in commercial products vary somewhat but are usually around an equal molar ratio of NH_4 and S, which provides a product characterized as 20-0-0-40 (Table 1). It is corrosive, strongly alkaline (pH > 10) and generates fumes of both H_2S and NH_3. The material must be kept in a closed system made of stainless steel or black iron, but not in copper-containing alloys such as brass or bronze. Ammonium polysulfide is a strong reducing agent.

Another compound allied with ammonium polysulfide is ammonia-sulfur, which is produced by dissolving or suspending powder or colloidal sulfur into liquid anhydrous ammonia (Phillips and Scott, 1996). A commercial product may contain a typical composition of 74-0-0-10. This product has not been used extensively due to certain application difficulties associated with thiosulfate precipitation.

Calcium polysulfide, CaS_x, is manufactured by reacting H_2S with calcium hydroxide at a Ca to S molar ratio of about 1 to 3. A commercial product may contain 24% sulfur and 9% Ca. This product is also strongly alkaline but acts as an acidulant upon sulfide oxidation in soils.

3. Sulfates of Iron and Aluminum

These granule products are among the oldest soil acidifiers and have the advantage of ease of handling compared to strong acids. However, the quantities required to achieve sufficient dissolution of $CaCO_3$ are substantially greater than most other products (Table 1), so that these products suffer from high costs of transportation. Another old product, $(NH_4)_2SO_4$, is still used widely, but mostly as a N-fertilizer rather than as a soil amendment with soil conditioning value.

C. Acidic Gases

1. Sulfur Dioxide

Sulfur dioxide (SO_2) used for conditioning irrigation water is usually produced by burning elemental sulfur on site with specialized equipment. The SO_2 is then injected into irrigation water. The use of SO_2 is confined mostly to some areas of California (Leclercq et al., 1972).

2. Carbon Dioxide

Carbon dioxide (CO_2) generated through the combustion of fuel at irrigation pump stations can, in theory, be scrubbed with water to prevent Ca precipitation. However, the solubility of CO_2 in water is low, and little is documented

about its effectiveness as a conditioner of alkaline water. Carbon dioxide, however, plays a major role in $CaCO_3$ dissolution in soils.

III. REACTIONS OF ACIDS AND ACIDULANTS IN ALKALI SOILS AND WATER

A. Reactions in Water

1. Dissolution

Strong acids (H_2SO_4, and H_3PO_4), and acid blends (urea/sulfuric acid and urea/phosphoric acid) dissociate almost instantaneously in irrigation water, releasing H^+, urea, plus the anions. The dissolution of these compounds is exothermic, creating considerable heat at the point of contact with water. The dissolution of polysulfides into irrigation water generates sulfur plumes of milky appearance. Sulfides precipitate as colloidal S, as pH decreases from the original level of about 10, whereas ammonium and Ca ions dissolve readily into water.

Acidic gases (SO_2 and CO_2) dissolve into water and form sulfurous acid or carbonic acid.

$$SO_2 + H_2O \Leftrightarrow H_2SO_3 \Leftrightarrow 2H^+ + SO_3^{-2} \quad (1)$$

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (2)$$

The dissociation constant of H_2SO_3 is much higher than that of H_2CO_3.

2. Neutralization Reactions

Hydrogen ions dissociated from acids or dissolved acidic gases react readily with OH^-, either initially present in the water or added in the form of ammonium hydroxide or ammonia gas.

$$NH_4OH + H^+ \Leftrightarrow NH_4^+ + H_2O \quad (3)$$

3. Reactions with Carbonates

Hydrogen ions also react with carbonate species, primarily HCO_3^- present in alkali irrigation water, and convert them to carbonic acid.

$$H^+ + HCO_3^- \Leftrightarrow H_2CO_3 \quad (4)$$

Under a system open to the atmosphere, carbonic acid decomposes to CO_2 and H_2O as shown by the reverse reaction of Eq. (2). The pH of the water remains above neutral, until about 90% of the HCO_3^- ions present are converted to H_2CO_3, and eventually to CO_2 and H_2O (Miyamoto et al., 1975b). The concentration of H_2CO_3 in an open system is largely fixed by the partial pressure of CO_2. Under a closed system, which may exist in water flowing through

water-filled pipes or tubes, carbonic acid accumulates in the system. This causes the pH of the water to drop below neutral, even when the acid application is as low as 10% of the concentration of HCO_3^- (Miyamoto et al., 1975b).

When Ca ions are present in the water, the reduction in HCO_3^- concentration reduces Ca precipitation.

$$Ca^{++} + 2HCO_3^- \Leftrightarrow CaCO_3 (\downarrow) + H_2CO_3 \quad (5)$$

or

$$Ca^{++} + NH_3 + HCO_3^- \Leftrightarrow CaCO_3 (\downarrow) + NH_4^+ \quad (6)$$

The reaction given by Eq. (5) is strongly dependent of the partial pressure of CO_2 in gas phase. The precipitation of Ca in ammoniated water is extensive and nearly instantaneous (Miyamoto and Ryan, 1976).

B. Reactions in Soils

1. Hydroxylation

Iron or aluminum sulfates, which are usually applied directly to soils, undergo hydroxylation in contact with water and release H^+.

$$FeSO_4 + 2H_2O \Leftrightarrow Fe(OH)_2 + 2H^+ + SO_4^{-2} \quad (7)$$

$$Al_2(SO_4)_3 + 6H_2O \Leftrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{-2} \quad (8)$$

These reactions allow H^+ to react with soil carbonates, principally $CaCO_3$ and Na_2CO_3 if present. Both Fe and Al hydroxides precipitate in calcareous or alkali soils.

2. Oxidation Reactions

Elemental S applied to the soils is subject to microbial oxidation through the activity of Thiobacillus.

$$S + 3/2\ (O_2) + H_2O \Leftrightarrow 2H^+ + SO_4^{-2} \quad (9)$$

The rate of oxidation is affected by soil moisture, soil temperature, and the surface area (or particle sizes) of elemental S. The oxidation of S requires elevated soil temperatures, typically above 25°C, and preferably as high as 40°C (Paulina, 1951), and wet to moist soils with a soil water suction range of 0.01 to 0.1 bar (Moser and Olson, 1953). The rate of oxidation increases with the fineness of S particles (Burns, 1967), and upon wetting and drying (Haynes, 1928). A powder form of S can be oxidized in several months, whereas flake sulfur may require a year or more for oxidation, especially in sandy dry soils with little organic matter. The oxidation of large S particles (>0.4 mm) may be enhanced by inoculation with *Thiobacillus thiooxidans* (McCaskill and Blair, 1987).

The oxidation of sulfides, applied either as NH_4S_x or CaS_x, is believed to be considerably faster than that of elemental S because of its colloidal size, provided that soil conditions are favorable for Thiobacillus activities. In order to satisfy the comparatively high soil moisture requirement for oxidation, colloidal sulfur, which forms in irrigation water through the application of sulfides, must penetrate into the soil to some depth. This requirement is usually met when these products are applied to plowed and disked fields.

Urea or ammonium applied with sulfuric or phosphoric acid is also known to undergo microbial oxidation to NO_3^-, which generates H^+ (e.g., Morrill and Dawson, 1967).

$$NH_4^+ + 2O_2 \Leftrightarrow NO^-_3 + 2H^+ + H_2O \quad (10)$$

Prior to nitrification, urea must be first decomposed to NH_4^+ through urease activities, and this reaction usually begins in a matter of several days in the presence of organic matter. The microsoil environments adjacent to urea temporarily become alkaline (Fenn and Miyamoto, 1981).

3. Dissolution of Soil Carbonates and Oxides

Hydrogen ions (H^+) present in excess of neutralizing NH_4OH or HCO_3^- react with soil carbonates.

$$CaCO_3 + 2H^+ \Leftrightarrow Ca^{+2} + H_2CO_3 \quad (11)$$

The extent of dissolution depends on the system in question. Under an open system, two moles of H^+ are usually required to dissolve one mole of $CaCO_3$, and H_2CO_3 is decomposed to CO_2 and H_2O. In a closed system, H_2CO_3 can release additional Ca (Miyamoto et al., 1975b).

Once soil carbonates are removed, hydrogen ions react with oxides (or hydroxides) of Fe and Al. Al and Fe oxides help develop stable oil aggregates under low pH, but not necessarily under alkaline conditions (Vodyanitskiy and Dokuchayev, 1985). Some DTPA extractable Mn and Fe may appear at acid application rates below the neutralization point, but water soluble Mn, Zn and Fe appear mostly after the complete removal of soil carbonates, usually in the order of Mn, Zn, then Fe (Ryan et al., 1974).

IV. ACID AND ACIDULANT APPLICATION FOR CONDITIONING IRRIGATION WATER

The concern over the use of sodic water on irrigated lands is probably best characterized by the statement of Scofield and Headly (1921): "Hard water makes soft land, and soft water makes hard land". Soft water rich in sodium carbonate tends to disperse soil particles and lowers aggregate stability and soil perme-

ability. Carbonates in water have been recognized as a factor contributing to soil structural degradation as they precipitate Ca (Eaton, 1950). In spite of these well-established facts, the use of acids for water conditioning had been discouraged by some, partly because of the concern that acid applications might corrode irrigation systems and partly because of handling difficulties. With the introduction of drip irrigation systems, this perception has changed, and acid and acidifying N fertilizer applications became a common practice to reduce emitter clogging (Gilbert et al., 1979). Likewise, the use of acid or acid-based N fertilizers for altering sodicity of irrigation water became a common practice in surface irrigated areas (Stroehlein et al., 1978). The type of irrigation water treated today is no longer confined to "soft" water, but includes some "hard" ones.

A. Treatments for Preventing Ca Precipitation

1. Amendment Requirements

The quantity of acids, acid blends, or acidic gases required to prevent Ca precipitation is highly dependent upon the system in question. In a system open to the atmosphere, it equals the acid required to convert about 90% of HCO_3^- to CO_2 and H_2O, and it is practically independent of Ca concentrations. At the rate of acid application, the pH of the water remains above neutral. However, once the acid concentration exceeds the equivalent concentration of HCO_3^-, the pH of the water sharply drops below neutral (Miyamoto et al., 1975b). Table 2 shows examples of acids or acidic gas (SO_2) required to prevent Ca precipitation.

The quantities of acids, acid blends, and acid gases required to prevent Ca precipitation under a closed system are low, usually no more than 10% of the equivalent concentrations of HCO_3^-. The requirement is further reduced with decreasing Ca concentrations in the water. Acid applications exceeding about 10% of HCO_3^- concentration in a closed system bring the pH of water below 7, but not below 6, until the acid application reaches about 90% of the HCO_3^- concentrations (Miyamoto et al., 1975b).

When NH_3 or NH_4OH is to be applied simultaneously, the quantity of acid required will increase by the equivalent concentration of NH_3 or NH_4OH (Miyamoto and Ryan, 1976). Acids or acidic gases applied to ammoniated irrigation water not only prevent Ca precipitation but also reduce ammonia volatile losses from irrigation water and soil surfaces (Miyamoto et al., 1975d). Table 2 includes the concentration of H^+ and quantities of acid, acid blends, or SO_2 required to prevent Ca precipitation in ammoniated irrigation water.

2. Application Systems

Open Ditch Flow. Acid applications to open irrigation ditches are usually made from a storage tank through flexible tubing. Since the density of acid is considerably greater than that of water (Table 1), acids tend to settle to the bot-

Table 2 Quantities of Acids and Acidic Gases Required to Prevent Ca Precipitation in Irrigation Water

Conditions	HCO^-_3 or NH_3 mg L^{-1}		Acid Required[a]			
			H_2SO_4[b]	H_3PO_4[b],	Urea-acid[c]	SO_2
Open system			mg L^{-1}			
	50	0	38	34	62	24
	100	0	76	68	124	47
	150	0	114	103	184	71
	200	0	152	137	248	94
	250	0	190	172	308	118
Closed system (approximate)						
	50	0	3	3	6	2
	100	0	7	6	12	4
	150	0	11	10	18	7
	200	0	15	13	24	9
Open and closed systems						
	0	25	76	69	123	47
	0	50	152	137	246	94
	0	75	228	206	370	141
	0	100	304	275	493	188

[a]Expressed in mg L^{-1}, which equals kg per 10 cm water × ha.
[b]The concentration of sulfuric acid was assumed to be 95% and that of phosphoric acid 70%.
[c]Assumed to contain 1 mole of urea and 1 mole of H_2SO_4.

tom of the ditch, especially at a low flow rate. This problem is usually alleviated through acid applications to a turbulent flow portion or by providing a simple device to enhance mixing. Acid storage tanks should be placed in a manner whereby accidental spills can be contained. The most common incident of acid spills is caused by valve or joint failures. Care must also be taken to avoid water entry, including water vapor condensation in an empty storage tank, which can cause a violent reaction in contact with acids.

Pipe Flow. Acid applications to pressurized pipe flow require a corrosion resistant injection device commonly used for liquid fertilizer injection. In the case of drip irrigation systems made of plastic materials, acids can be applied with little concern for corrosion. The precipitation of Ca generally occurs at emitters where the water is exposed to the atmosphere. In sprinkler systems made of Al or copper containing alloys, acid application is not recommended, unless reliable precision application systems for NH_3 and H_2SO_4 are available or these chemicals are premixed in a water reservoir.

B. Treatments for Reducing Sodicity and Soil Structural Degradation

1. Reducing Sodicity

The use of acids and acidulants for reducing sodicity can be classified into two types. The first type is to reduce sodicity of irrigation water (and consequently that of the irrigated soils), and the second type is to reduce sodicity of surface soils. The first type is usually used when sodicity of irrigation water is high enough (or salinity of the water is too low) to cause soil structural degradation, unless amended constantly, or NH_3 (or NH_4OH) is applied through water. The second type is used to keep sodicity of surface soils in check when irrigation water has salinity sufficient to avoid serious structural degradation of the soils without constant application.

The quantities of acid, acidic gases, or acid blends required to prevent an increase in sodicity (associated with Ca precipitation) are similar to those used for preventing Ca precipitation discussed earlier (Table 2). At that rate of amendment application, both the sodium adsorption ratio (SAR) and the salinity of water remain the same as those of the irrigation water prior to Ca precipitation. Hydrogen ions are consumed for decomposing HCO_3^-, and SO_4^{-2} or PO_4^{-3} ions take the place of HCO_3^-. Acids or acidic gas applications to irrigation water are thus to prevent an increase in sodicity of irrigation water or a reduction in salinity associated with the precipitation of Ca^{+2} and HCO_3^- (Table 3). When NH_3 (or NH_4OH) is applied with acids or acidic gases, however, sodicity of the surface soil is actually reduced following NH_4^+ oxidation to NO_3^-. The use of

Table 3 Changes in Sodium Adsorption Ratio (SAR) of Irrigation Water Following Aeration, Ammonia Application, and Ammonia Plus Sulfuric Acid Application

Water sources Location	Well Gila Bend	Well Safford	Salt R Phoenix	Colorado R Yuma
Initial quality				
Salinity (dS m^{-1})	2.39	0.74	1.25	1.1
Ca^{+2} (meq L^{-1})	3.2	2.5	1.0	4.4
HCO_3^- (meq L^{-1})	3.7	2.8	2.7	2.7
Sodicity (SAR) changes				
Initial	13.8	7.2	6.3	2.3
Aeration[a]	17.	9.5	7.6	2.4
with NH_3 (50 mg L^{-1})	26	12	10	3.6
with $NH_3 + H_2SO_4$ (100 mg L^{-1})	20	9.5	8.1	3.0

[a]Increase in SAR associated with aeration is commonly referred to as HCO_3 effects.
Source: Miyamoto and Ryan, 1976.

urea-acid blends follows the same principle, but their ability to reduce sodicity of soil surfaces is lower than that of ammonium-acid mixtures, because uncharged urea moves into the soil profile following the wetting front, and the acid release potential of urea is less than NH_4^+. Nonetheless, acids used as a solvent of urea help prevent Ca precipitation in irrigation water and an increase in sodicity of the soil (Ali, 1989).

Ammonium or calcium polysulfide applied through water does not prevent Ca precipitation in irrigation water, but it helps reduce Ca precipitation in soils or, if applied in excess of the concentrations of HCO_3^- in irrigation water, it can solubilize soil $CaCO_3$ when sulfides are oxidized to SO_4^{-2} or NH_4^+ is oxidized to NO_3^-. The oxidation of S and NH_4^+ or the addition of Ca through Ca polysulfide applications can help lower sodicity of the surface soils.

An alternative to water application is the direct soil application of acids and acidulants. These are discussed later in the section dealing with reclamation of sodium-affected soils. Water application is usually more efficient if the water is sodic, or low in salinity, and improvements in water infiltration is the primary goal. However, if the goal is to lower soil sodicity, soil hardness, or crusting, soil application of sulfuric acid, phosphoric acid, urea-phosphoric acid, iron sulfate, or sulfur provides options.

2. Improving Soil Permeability

Hydraulic Conductivity. The primary goal of reducing sodicity of irrigation water and/or surface soils is usually to obtain improved water transmission through the soils. There are several studies that evaluated the effectiveness of these compounds in improving the saturated hydraulic conductivity, but the results are rather mixed, especially in water having salinity greater than about 1 dS m^{-1}. A laboratory percolation test performed with three soils from the San Joaquin Valley, California, using water having low salt (EC = 0.05 and 0.7 dS m^{-1}) and low sodium (SAR = 0.4 and 1.7), has shown significant increases in percolation rate when SO_2 or gypsum was applied to the water (Mohammed, 1972). However, the response to Ca polysulfide applications was inconsistent, and at times hydraulic conductivity decreased with increasing application rates, presumably because of pore plugging caused by precipitated colloidal sulfur. In addition, the extent of percolation improvements depended on soil types. A similar laboratory study conducted with five soil types from southern Arizona using four types of simulated irrigation water having a salinity range of 0.7 to 3.5 dS m^{-1} has shown that sulfuric acid applied at a rate equal to approximately 90% of the HCO_3^- concentrations in chemical equivalents provided significant improvements in percolation rates in some soils only when the SAR of the irrigation water was higher than 7.9 (Gumaa et al., 1976). In a simulated water having salinity of 0.7 dS m^{-1} and a SAR of 9.7, the percolation rate increases ranged from 12 to 66% depending on soils. In saline sodic water having salin-

ity of 3.5 dS m^{-1} and sodicity of 10.5, the increase ranged from 0 to 14%. In moderately saline water having salinity of 1.1 dS m^{-1} and sodicity of 7.9, the increase over nontreated ranged from none to 48%, depending on soil type. There seemed to be no definite correlation between hydraulic conductivity improvements and clay minerals. The difference in hydraulic conductivity among the five soils varied by a factor of 5, while the difference among the different water sources was within a factor of less than 2.

Judging from these results, the saturated hydraulic conductivity is primarily a function of soil types and salinity of irrigation water. When salinity of irrigation water is low, e.g., less than 1 dS m^{-1} and the soil is dispersible, acids or polysulfide treatments of irrigation water are likely to yield a significant increase in saturated hydraulic conductivity, especially when the SAR exceeds about 7. This general guideline is consistent with other observations of water quality effects on saturated hydraulic conductivity.

Water Infiltration. Water infiltration into irrigated soils is usually affected by water quality more sensitively than saturated hydraulic conductivity (Oster and Schroer, 1979). The reasons include soil aggregate destruction and soil particle dispersion induced by slaking of dry soils and physical force of water (Abu-Sharar et al., 1987; Shainberg and Letey, 1984). Another reason relates to precipitation of Ca at the soil surface when salts are brought to the soil surface through upward capillary flow. This process can increase sodicity of the soil surface many times greater than that of irrigation water or the soil solutions below the surface, especially in sandy or loamy soils with low cation exchange capacities (Miyamoto and Cruz, 1987). All these contribute to the formation of a thin layer of soil having reduced permeability at the soil surface, which then becomes a flow-limiting layer during water infiltration.

Application of acids, acidic gases, or acidulants is a way to minimize soil structural degradation and associated reductions in water infiltration. In a field infiltration test under ponding, acid applications at a rate of 2.2 meq L^{-1} to low-salt and high-sodium water (EC = 0.62 dS m^{-1} and SAR = 30) produced a 75% increase in water infiltration rate into irrigated silt loam soil (Miyamoto and Stroehlein, 1975). In a similar field test with low-salt and low-sodium water (EC = 0.42 dS m^{-1} and SAR = 2.5), infiltration improvement was not significant (Stroehlein et al., 1978). Application of acid to ammoniated water increased the infiltration rate of low salt water (EC = 0.6 dS m^{-1} SAR = 8.9) by 28 to 83% depending on soils (Miyamoto and Ryan, 1976). The effect of the acid treatment of ammoniated water persisted in subsequent irrigations without any chemical additives, probably because of NH_4 oxidation which releases Ca in calcareous soils.

Water infiltration responses to chemical treatments of water vary with the compound used. In a field infiltration experiment performed in the Imperial Valley of California, water applications of ammonium polysulfide and sulfuric

acid at a sulfur rate of 70 kg ha^{-1} provided infiltration increases of 28 and 13%, respectively (Robinson et al., 1968). The quality of the irrigation water used was not given, but the Colorado River water at the location usually has an EC of 1.0 to 1.4 dS m^{-1} and a SAR value of 2 to 6. In the same test, calcium polysulfide applied at a sulfur rate of 70 kg ha^{-1} did not produce any significant increase, which is consistent with the finding from laboratory hydraulic conductivity measurements mentioned earlier. Pore plugging caused by sulfur precipitation is believed to have masked out the effect of calcium polysulfide.

In a subsequent field infiltration test at the same location, ammonium polysulfide applied through water at a S rate of 70 kg ha^{-1} provided a twofold increase in infiltration rate, while ammonium nitrate applied at an equivalent rate yielded only a 10% increase. However, neither treatment gave any residual effect when untreated water was subsequently applied. The small increase in infiltration rate observed from sulfuric acid or ammonium nitrate treatments in these tests is within the range commonly observed for this type of water. The superior performance of ammonium polysulfide treatment is beyond the range that is ordinarily expected under nonsodic conditions, and it led the authors to conclude that the increase was evidently caused by a unique property of this compound, which is not yet understood.

In our recent laboratory infiltration experiments, water application of ammonium polysulfide, when compared to $CaCl_2 \cdot 2H_2O$, urea/acid, or ammonia/acid applied at a chemically equivalent rate, did not produce any superior results (Table 4). Instead, the effect of NH_4S_x was similar to that of ammonia/sulfuric acid mix. Improvements in infiltration rates from any of the chemical amendments were fairly small, as can be expected from the types of water tested. The Rio Grande water is low in sodicity, whereas the test water from Pecos had high salinity to counter the elevated level of sodicity. This experiment, however, does not rule out the possibility of improved water infiltration into dry soils with an application of ammonium polysulfides, which are widely speculated to have a property of improving soil wettability. This experiment seems to indicate that NH_4/sulfuric acid and ammonium polysulfides can improve water infiltration as much as, if not more than, the equivalent concentration of $CaCl_2 \cdot 2H_2O$. It seems that the choice of water conditioning chemicals must include nitrogen values.

From a basic research point of view, the effect of pH on soil permeability warrants additional study. A laboratory permeability study involving three noncalcareous soils in California indicates that Na-induced hydraulic conductivity reductions in low salt water (e.g., EC < 1 dS m^{-1}) at a SAR of 20 can be prevented by lowering the pH to 6.0 (Suarez et al., 1984). One possible reason is thought to be the changes in soil particle bonding orientation when the charge characteristics of oxides of Fe and Al and kaolinite change from negative to positive with lowering pH. The positively charged oxides and kaolinite can form a

Table 4 The Depth of Water Intake of Chemically Treated Water into Saneli and Hoban Silty Clay Loam when the Intake of Unconditioned Water Reached 10 cm

Water sources Location	Chemicals added	Rio Grande El Paso		Well Water Pecos	
EC (dS m^{-1})		1.1		3.9	
SAR		3.5		14.2	
pH		8.3		7.9	
Soil types		Saneli S.C.L.		Hoban S.C.L.	
Soil conditions		Moist	Wet	Moist	Wet
Chemicals	meq L^{-1}	Intake Depth (cm)			
None	0	10.0	10.0	10.0	10.0
$CaCl_2$	3.8	10.8	11.6[a]	10.6	10.9
Urea/H_2SO_4	3.8	—	—	10.5	10.6
NH_4/H_2SO_4	3.8	10.5	11.6[a]	11.6[a]	11.6[a]
NH_4S_x	3.8	11.5[a]	11.2	11.7[a]	11.6[a]
PAM (ppm)	5.0	10.7	11.3	11.8[a]	11.9[a]
$CaCl_2 \cdot 2H_20$	7.8	—	—	11.6[a]	11.0
$CaCl_2$ Soln	38.0	11.5[a]	11.7[a]	11.7[a]	11.7[a]

[a]Significant at a 5% level.
Source: Unpublished data, author's laboratory.

bond with the negatively charged clay particles. Another possible reason relates to a reduction in the thickness of the diffused double layer with lowering pH. In calcareous soils, the pH reduction caused by acidification is buffered. However, the pH of water in subsurface drip systems and soil solutions can be reduced below neutral when carbonic acid accumulates. The pH of irrigation water high in sodium carbonate or injected with ammonia ranges from 9 to 10, which is readily reduced with acid to near neutral. Under these circumstances, reported increases in soil permeability or water infiltration with acid application may be partly accounted for by lowering pH, besides preventing Ca precipitation.

A recent field infiltration study conducted on noncalcareous sandy loam (pH = 6.3) in California, however, indicated that water infiltration improvements obtained through water application of Ca acetate, Ca nitrate, and Ca chloride seemed to have increased with increasing pH of the soils from 6.3 to a range of 6.7 to 7.3 (Wildman et al., 1988). These Ca compounds were applied to low salt water (0.1 dS m^{-1}) at a rate of 3 meq L^{-1}. The reason for this behavior is not clear but seems to be related to the increase in Ca retention in surface soils presumably due to the increase in the cation exchange capacity caused by the modest increase in pH.

From a practical point of view, several aspects warrant some attention. One relates to the assessment of the need for water conditioning. This may include the effect of water conditioning on infiltration of rain water, which has not yet been studied adequately. In assessing the need for water conditioning, salinity control is also a part of the picture in saline areas. Even a small improvement in infiltration rates can affect the salt balance in the root zone. Water testing for salinity, sodicity, and pH certainly helps, but water infiltration or penetration should be field-tested to verify the effectiveness of the intended conditioning. Compacted soils, for example, usually respond very poorly to chemical treatments (Baumhardt et al., 1992) until the compaction is removed by physical means. Sodding or cropping can also alter infiltration response to chemical treatments. Another aspect relates to selection of chemical amendments. From the view of containing production costs, it seems that greater attention should be given to the use of NH_4 containing acid fertilizers as a source for water conditioning. The frequency of chemical application is another issue. The current indication is that low salt water requires constant treatment unless the compound provides sufficient and steady release of H^+ at the soil surface. This requirement, however, can change with the addition of polyacrylamide, which is known to provide some persisting effects as discussed in a separate chapter (15). There is, of course, the bottom line question of how to project crop response to water conditioning. A rule of thumb is that a positive response is likely if there is clear evidence to indicate that water and/or salt stress related to poor water infiltration and penetration are limiting crop performance. Much-publicized effects of lowering pH of water and resulting increases in crop performance are, however, questionable at best in most calcareous soils, unless the pH of water is well above the equilibrium pH of $CaCO_3$ systems.

V. ACID AND ACIDULANT APPLICATION FOR RECLAIMING SODIC SOILS

The soils containing high levels of exchangeable Na are found widely both in irrigated and nonirrigated lands or arid and semiarid regions of the world. Most of these soils are calcareous or alkaline, although some sodic soils are acidic at times. In either case, poor soil permeability induced by high levels of exchangeable Na presents a major obstacle for reclamation that involves not only the replacement of Na but also the leaching of replaced Na and soluble salts. Chemical amendments, especially gypsum, were recognized to help reduce exchangeable Na and improve water infiltration necessary for reclamation. Acids and acidulants were thus originally considered simply as an alternative or a substitute for gypsum, as they convert $CaCO_3$ to Ca^{+2} and SO_4^{-2} in sodium-affected calcareous soils.

Subsequent studies, however, have shown that acid treatments can result in a greater crop response than gypsum treatments under certain conditions. The

primary reason seems to be related to improved availability of certain plant nutrients, especially micronutrients and phosphorus (Stroehlein et al., 1978). Recent studies have also shown that in highly sodic alkaline soils, soil application of sulfuric acid can provide significantly better water infiltration and crop response than gypsum application (Miyamoto and Stroehlein, 1986). We will review and examine these unique characteristics of acids and acidulants as amendments for reclaiming sodic soils.

A. Reclamation of Moderately Sodic Calcareous Soils

Moderately sodium-affected calcareous soils with exchangeable Na percentages (ESP) of 15 to 35% are readily reclaimed for crop production, provided that soil texture is not impervious clay and that drainage outlets are available. Indeed, the current reclamation activities in the western USA deal primarily with this type of soil. The target of the reclamation is to lower exchangeable Na and to improve water infiltration necessary for leaching. In some cases, acids or acidulants may be applied for a dual purpose of lowering ESP and improving nutrient availability in Na-affected calcareous soils.

1. Acid and Acidulant Requirements

Reducing Exchangeable Na. For the removal of exchangeable Na, $CaCO_3$ present in the soils must first be solubilized with acids or acidulants as discussed earlier. Once Ca is solubilized, it undergoes the well-known exchange reaction.

$$Ca^{2+} + 2\ NaX \Leftrightarrow CaX_2 + 2Na^{+} \tag{12}$$

where X denotes the cation exchange sites. This reaction is largely governed by the law of mass reaction, and one mole of Ca added may or may not replace two moles of exchangeable Na, depending on the dissolved cation concentrations and the exchange constants. For simplicity, however, the quantity of amendments required to replace the exchangeable Na is computed with an assumption of quantitative replacement.

$$AR = (ESP_0 - ESP)\ CEC\ (\alpha\rho\ D) \tag{13}$$

where AR is the quantity of acids or Ca required to replace exchangeable Na to a soil depth of D, ESP_0 the initial exchangeable Na percentage, ESP the target exchangeable Na percent, CEC the cation exchange capacity, ρ the soil bulk density, and α the unit conversion factor, which is 100 if AR, ESP, CEC, ρ, and D are expressed in eq ha^{-1}, %, eq kg^{-1}, kg m^{-3}, and m, respectively. The amendment required in terms of material weights per ha can then be estimated by multiplying applicable equivalent weights shown in Table 1.

The target ESP is traditionally considered to be 15%. However, it usually requires some adjustments depending on soil type, crops to be grown, water qual-

ity, and the irrigation system used. The depth of the soils to be reclaimed is somewhat arbitrary but is usually referenced to the depth of the major root zone. The estimated acid requirements to lower ESP_0 to 10 and 15% from the assumed depths of the soils with a CEC of 0.25 eq kg^{-1} are shown in Table 5. In clayey soils with a greater CEC, the requirement increases in proportion to the CEC. According to the estimates, the amendment required (expressed in H_2SO_4 equivalent) is in the range of 2.5 to 13 Mg ha^{-1} in moderately sodic soils with an ESP of 30%. In highly sodic soils or in clayey soils with a greater CEC, the estimated quantities may become impractically large. In such cases, alternative methods of reclamation may be required as discussed later.

The above procedures, originally developed for Ca compounds, are adapted here for acids and acidulants with an assumption that one mole of acids or acidulants solubilizes one mole of Ca from $CaCO_3$. This assumption is realistic in an open system where the acid and carbonate reactions take place at the soil surface following ground applications. In the case of sulfur incorporated into moderately sodic calcareous soils, a greater quantity of Ca can be solubi-

Table 5 The Quantities of Acids, Acidulants, and Gypsum (All Assumed to be 100% Ingredient) Required to Lower the Exchangeable Na Percent (ESP) to Desired Levels from Various Soil Depths at a Cation Exchange Capacity of 0.25 eq kg^{-1}

Initial ESP	Target ESP	Amendment types	Quantities required for soil depths		
			15	30	60 cm
%	%		Mg ha^{-1}		
30	15	H_2SO_4	2.5	5.0	10.1
		NH_4S_x[a]	1.3	2.6	5.1
		S	0.8	1.6	3.3
		$CaSO_4 \cdot 2H_2O$	4.4	8.8	17.6
		$FeSO_4 \cdot 7H_2O$	7.1	14.2	28.4
30	10	H_2SO_4	3.3	6.6	13.2
		NH_4S_x[a]	1.7	3.4	6.8
		S	1.1	2.2	4.3
		$CaSO_4 \cdot 2H_2O$	5.6	11.6	23.2
		$FeSO_4 \cdot 7H_2O$	9.4	18.7	37.4
50	15	H_2SO_4	8.5	17.6	35.3
		S	2.8	5.6	11.1
		$CaSO_4 \cdot 2H_2O$	14.9	29.8	59.7
70	15	H_2SO_4	15.1	30.2	60.4
		S	4.9	9.8	19.7
		$CaSO_4 \cdot 2H_2O$	26.5	53.0	106.0

[a]The contribution of NH_4 oxidation is included, and the product assumed is NH_4S.

lized, at least in theory, because of soil entrapment of CO_2. This possibility, however, has not yet been fully verified, partly owing to highly variable oxidation rates of elemental S.

Improving Water Infiltration. The quantities of acids or acidulants required to improve water infiltration are usually superseded by the quantities required for Na replacement. However, the idea of computing the amendment requirements based on permeability improvements, instead of Na replacement, has merits in reclamation of highly sodic soils where the amendment requirements for Na replacement become impractically large. This topic is discussed later. Even in moderately sodic soils, this concept may deserve some attention when nonsodic saline water is to be used for irrigation. Under such circumstances, the exchangeable Na can be replaced eventually, as long as amendments are applied at a quantity needed to maintain water infiltration. The quantity of amendments required to maintain water infiltration is soil dependent, and usually 2 to 5 Mg ha^{-1} in moderately sodic soils.

Improving Nutrient Availability. The quantities of acids or acidulants required to improve availability of certain micronutrients and phosphorus are usually determined empirically. As demonstrated by Ryan et al. (1974), it requires almost a complete removal of $CaCO_3$ to release most micronutrients, although this rule does not seem to apply to phosphorus. Acid applications usually solubilize Ca-bound phosphorus, but not Fe or Al-bound phosphorus (Khorsandi, 1994). In most calcareous soils, large quantities of acids or acidulants are required if one attempts to dissolve $CaCO_3$ from the entire root zone. (Note that it will require 10 Mg ha^{-1} of sulfuric acid to remove $CaCO_3$ from 1 cm of soil layer containing 7.5% $CaCO_3$ by weight.) However, experience has shown that the removal of $CaCO_3$ from a small portion of the root zone is usually sufficient to provide necessary micronutrients (e.g., Wallace and Mueller, 1978; Fenn et al., 1990). The quantities of acids and acidulants necessary for sufficient release through soil injection of sulfuric acid typically range from 0.5 to 2 Mg ha^{-1}, which are usually lower than those required for Na replacement in calcareous sodic soils.

2. Amendment Application

The quantities of acids or acidulants required to reclaim sodic soils are usually too large to be applied through irrigation water, not only because the pH of water is reduced to the levels that pose corrosion hazard but also because of CO_2 entrapment in soil profiles, which slows water infiltration (Miyamoto et al., 1973). In addition, amendments applied through water usually result in a greater amendment application in permeable portions, and a lesser application in less permeable portions of the fields, which is not compatible with the objective of uniform reclamation. Thus amendments are usually broadcast directly to the soils or selectively to the portion of the field that requires most reclamation. Prior to amendment applications, soil compaction or petrogenetic pans,

which limit water infiltration and penetration, must be removed through appropriate mechanical or physical measures. Chemical amendments are not a substitute for chiseling or subsoiling.

Surface Broadcast Application. If sulfuric acid or phosphoric acid is to be applied, the ground surface has to be dry. Otherwise vigorous reactions with moist soils generate noxious acid fumes. During the ground application of strong acids, care must be taken to reduce acid splatters, especially in windy areas. Some custom applicators have used flexible tubing, instead of drip nozzles, to apply acid on the ground, and others have used a sheet of rubber around the spray boom to reduce splatters. As soon as acids are broadcast, the field should be irrigated without delay, or otherwise be disked. Exposure to ground-applied acid is the prime source of injuries. Bedding of acid-treated ground enhances solubilization of certain micronutrients and phosphorus in row crops but is usually not recommended for achieving uniform Na replacement and leaching until the acid-treated ground is irrigated. If the field is to be irrigated with mobile sprinkler systems, such as side-rolls or center pivots, acid-treated fields should be disked to avoid acid splatters onto the sprinkler systems. Needless to say, aluminum pipes should not be laid on acid-treated fields. If surface irrigation methods are to be used, double borders should be placed at low ends so as to contain acidic water in the case of accidental break-off of the primary borders. If surface irrigation systems are designed for tail water reuse, the acid-treated ground should be disked to avoid corrosion of the reuse system. If the tail water becomes acidic, injection of ammonia into the collection reservoir may be necessary prior to pumping for reuse. The acidic tail water may not be discharged to drain ditches.

Ground Injection. Soil injection of strong acids is preferred to surface broadcast applications in terms of lowering hazards from acid application and improving availability of micronutrients efficiently in calcareous soils. Soil injection also allows the use of SO_2 in a manner used for NH_3 injection into crop beds (Roberts and Koehler, 1965). However, acid or acidic gas injection to crop beds (used for improving availability of certain nutrient elements) lowers the uniformity of Na replacement and salt leaching. An injection device designed to apply acid at a shallow depth with close spacings on a flat ground is a good compromise. Alternatively, ground injection can be combined with water application of polysulfides to improve the coverage of amendment applications.

3. Performance of Amendments

Reducing Exchangeable Na. It was noted earlier that the efficiency of Na replacement is subject to the law of mass reactions. Experimental data obtained from surface-applied amendments indicate that the removal of exchangeable Na by dissolved Ca is curtailed in saline sodic soils, owing to the presence of high concentrations of dissolved Na initially present plus those replaced from the exchange sites. With the leaching of the dissolved Na, the exchange reaction then

proceeds in a more efficient manner, provided that soluble Ca compounds are left at the soil surface. Soil column experiments have shown that the quantities of exchangeable Na replaced after leaching with 1.5 pore volume of water amounted to 79 to 100% of the Ca (or H_2SO_4) added to the soils as amendments plus those present in irrigation water (Table 6). These numbers, however, include the exchangeable Na removed by leaching alone without chemical additions. If the fraction is subtracted, the exchangeable Na removed amounted to 42 to 84% of the Ca added as amendment. An additional quantity of exchangeable Na may be removed through leaching by the process known as the dilution effect.

The replacement of Na is greater near the soil surface, and it becomes negative below certain depths due to Na translocation to deeper depths (Miyamoto et al., 1975c). Consequently, a typical pattern of exchangeable Na distribution after chemical applications and leaching is lowest near the soil surface. The ESP of the top 10 cm of soils can be lowered to as low as 5% when acids are broadcast with an intent to reduce the ESP to a range of 10 to 15% from the top 30 cm (Miyamoto et al., 1975c; Miyamoto and Enriquez, 1990). The type of amendments used, except for elemental S, does not seem to affect this pattern to any significant degree. However, the small differences in ESP at the soil surface coupled with the difference in soluble salts left at the soil surface can make a significant difference in the rate of water infiltration and leaching during reclamation in structurally weak soils (Miyamoto and Enriquez, 1990).

Improving Water Infiltration. The rate of water infiltration directly affects the rate of reclamation and is an important factor in reclamation of poorly permeable soils. Water infiltration in moderately sodic soils (ESP = 11 to 25%) following broadcast applications of concentrated sulfuric acid at 3 to 5 Mg ha^{-1} has increased roughly twofold (Yahia et al., 1975). When application rates exceeded 5 Mg ha^{-1}, however, no added benefit was observed, and at an application rate of 10 or 15 Mg ha^{-1}, the rate of water infiltration was actually reduced in moderately Na-affected soils. This apparent reduction in water infiltration is often related to the formation of a thin soil layer developed by reprecipitation of Fe and Al when they are transported from the surface to the alkaline zone. The depth of acidified layers at an acid application rate of 10 Mg ha^{-1} extends 1 to 5 cm in soils having the titratable basicity of 100 to 20 kg m^{-3} or $CaCO_3$ contents of 7.5 to 1.5% by weight, respectively. Thus the flow restricting layer usually develops near the soil surface, and physical disturbance of this thin layer restores water infiltration. As mentioned earlier, CO_2 evolved as a result of acid reaction with $CaCO_3$ also interferes with water infiltration at high rates of acid application (Miyamoto et al., 1973).

According to a recent soil column study (Miyamoto and Enriquez, 1990), sulfuric acid broadcast and incorporated into 5 cm of moderately Na-affected soils provided about the same rate of water infiltration as powder gypsum in-

Table 6 Removal of Exchangeable Na with Application of Sulfuric Acid, Gypsum, and Calcium Chloride Followed by Leaching at 1.5 Pore Volume in Two Moderately Na-affected Calcareous Soils

Soil type	Amendment		Exch. Na removed eq kg^{-1}	Final ESP %	Removal ratio[a]	Leaching duration days
	eq kg^{-1}	Mg ha^{-1}				
Saneli silty clay loam (Initial ESP = 17.5%, exch. Na = 0.035 eq kg^{-1}) (CEC = 0.20 eq kg^{-1})						
H_2SO_4	10.7	4.3	12	11.5	1.0	13
$CaSO_4 \cdot 2H_2O$	10.7	7.5	10	12.5	0.85	13
$CaCl_2 \cdot 2H_2O$	10.7	6.4	10	12.4	0.84	24
Control	0.0	0	3	16.2	—	55
Glendale silty clay (Initial ESP = 13.7%, exch. Na = 0.049 eq kg^{-1}) (CEC = 0.36 eq kg^{-1})						
H_2SO_4	24.0	8.5	23	7.2	0.91	31
$CaSO_4 \cdot 2H_2O$	24.0	15.0	23	7.4	0.91	32
$CaCl_2 \cdot 2H_2O$	24.0	12.8	20	8.2	0.79	42
Control	0	0.0	13	10.0	—	>100

[a]Defined as the exchangeable Na removed by Ca added in chemical equivalent.
Source: Miyamoto and Euriquez, 1990.

corporated to the same depth at an equivalent rate (Table 6). The test soil was moderately Na-affected saline calcareous soil (CEC = 0.20 eq kg^{-1} ESP = 17.5% and EC_e = 6.0 dS m^{-1}), and the water used for leaching had a salt composition similar to that of the Rio Grande (EC = 1.1 dS $^{-1}$ and SAR of 3.5). The data also show that the soil application of $CaCl_2 \cdot 2H_2O$ at a chemically equivalent rate was not nearly as effective as acid or gypsum treatment, presumably due to rapid leaching of $CaCl_2 \cdot 2H_2O$ from the soil surface layer. A similar study involving another moderately Na-affected Glendale silty clay (CEC = 0.36 cq kg^{-1}, ESP = 14% EC_e = 6.0 dS m^{-1}) has shown essentially the same results (Table 6).

These soil column studies also included iron and aluminum sulfate treatments, incorporated to a depth of 5 cm at the same equivalent rate as sulfuric acid or gypsum. Iron and aluminum sulfate treatments provided infiltration rates similar to or slightly less than those from the gypsum or sulfuric acid treatment. Some other studies (e.g., Tobia and Pollard, 1958), however, indicate that aluminum sulfate applied to alkali or calcareous soils provided much higher infiltration rates than sulfuric acid applied through water at an equivalent rate. This is probably not a fair comparison, however. As indicated earlier, acid applied through water in excess of HCO_3 concentration generates CO_2, which interferes with water percolation. The flow of acidic water can completely cease when CO_2 is entrapped in a soil profile.

A field infiltration study conducted at Safford Arizona (Alawi, 1977) using a moderately Na-affected Pima clay loam (ESP of 20 to 25%) has shown twofold increases in infiltration rate when sulfuric acid was broadcast at a rate of 2.2 Mg ha^{-1} and leached with water having salinity of 0.51 dS m^{-1}. The effect of gypsum (a commercial grade) applied at an equivalent rate (3.8 Mg ha^{-1}) was not nearly as prounounced as the sulfuric acid treatment, probably due to a slower dissolution rate of commercial granule products as compared to powder gypsum (Keren and O'Connor, 1982). When saline water having an EC of 3.2 dS m^{-1} was used for leaching, the results were essentially the same, except that the infiltration rates were overall higher than in the case of low salinity water. In a separate field infiltration test performed in Arizona (Miyamoto and Stroehlein, 1975) using saline sodic Gothard clay loam (ESP = 15 to 18%, and EC_e = 10 dS m^{-1}), both sulfuric acid and powder gypsum applied at 5 Mg ha^{-1} of sulfuric acid equivalent rate doubled the infiltration rate (Table 7). The leaching water used had low salinity (5 meq L^{-1}) and a moderate level of sodicity (SAR = 5.7).

Judging from some of these reports, it appears that water infiltration during the initial leaching of moderately Na-affected soils can be improved by a factor of about 2 at acid application rates of 2 to 5 Mg ha^{-1}. These rates are roughly equal to or smaller than the acid requirements estimated for the Na replacement from the top 15 to 30 cm at the target ESP of 10 to 15%. In many of the soils tested, the actual ESP at and near the surface was reduced to much

Table 7 Effect of Sulfuric Acid and Gypsum Applications on Water Infiltration and Yields of Grain Sorghum in Gothard Clay Loam (ESP = 17%, CEC = 0.42 eq kg^{-1}, and EC_e = 10 dS m^{-1}) Under Field Conditions

Amendments	Rate Mg ha^{-1}	Infiltration cm d^{-1}		Sorghum head wt. kg ha^{-1}
		1st	2d	
No treatment	0	—	—	2000
Leaching only	0	9	8	3100
Sulfuric acid	3	19	17	8400
Sulfuric acid	5	21	20	7300
Gypsum (powder)	9	20	21	8000

Source: Stroehlein et al., 1978.

lower values, typically around 5%. The flow limiting layer for infiltration into plowed and disked sodic soils usually develops within the top 10 cm where aggregate breakdown occurs first (Miyamoto and Enriquez, 1990). Thus lowering ESP and maintaining elevated levels of salinity in the top layer is critical for maintaining water infiltration. Such requirements can be met with the surface application of sulfuric acid or sulfates of Ca, Fe, and Al, but not always with calcium chloride when applied at a rate commonly used.

Sustainability of adequate levels of infiltration after acid treatment is a separate issue and would depend to a large extent upon quality of irrigation water used, besides soil texture and compaction. If needed, water treatments discussed earlier will provide an option for infiltration maintenance. Soil application of elemental S is another option for maintenance, but the performance has been rather inconsistent (e.g., Overstreet et al., 1951; McGeorge et al., 1956). What is obvious is that the exchangeable Na should be lowered during reclamation at least to a depth of the plow layer. Otherwise, plowing will bring the soil with higher sodicity to the soil surface, thus reintroducing infiltration problems.

There must be a word of caution against indiscriminate uses of acids and acidulants. Ground application of sulfuric acid or gypsum, for example, has been practiced on orchard floor for the purpose of improving water infiltration. Orchard floors are usually highly compacted, and our study has shown that chemical amendments are of little value, unless the compacted soil is first dealt with using physical measures (Helmers and Miyamoto, 1990). Likewise, chemical amendments are usually of limited value in improving poorly permeable clays with low ESP.

Crop Response. Crop responses to acid or acidulant applications may result from a combined effect of reduced ESP, improved water infiltration, reduced salinity and alkalinity, and improved nutrient availability. In a greenhouse pot

experiment using two moderately sodic saline soils from Arizona (Pima clay loam, ESP = 23%, EC_e = 15 dS m^{-1}) and Gothard clay loam (ESP = 17% EC_e = 12 dS m^{-1}), sulfuric acid was broadcast at 10 and 3 Mg ha^{-1}, respectively, then were leached with two pore volumes of water before planting kidney beans (*Phaseolus vulgaris*). These treatments provided vegetative growth nearly equal to those obtained from nonsaline and nonsodic soil used as a control (Stroehlein et al., 1978). This simple experiment may indicate that these saline sodic soils can be reclaimed with acid applications and leaching to a level that salt and sodium sensitive crops, such as beans, can be grown satisfactorily. In another greenhouse experiment using the same soil, the effect of sulfuric acid broadcast at rates of 3 and 6 Mg ha^{-1} was compared against 7 and 10 Mg ha^{-1} rates of gypsum along with an Fe chelate application at 1 kg ha^{-1} using grain sorghum (*Sorghum bicolor*) as a test crop (Stroehlein et al., 1978). In Pima clay loam, sulfuric acid and Fe-chelate treatments provided greater vegetative growth than the gypsum treatment, indicating that the superior crop response from the acid treatments might have been a result of improved availability of Fe. The effectiveness of acids to improve Fe availability has been demonstrated in both greenhouse and field trials (e.g., Mathers, 1970; Ryan et al., 1975b). In Gothard silt loam with an adequate level of Fe, acid and gypsum treatments provided an equal crop response. In a subsequent field test on Gothard silt loam, both acid and gypsum treatments provided dramatic increases in sorghum yields (Table 7), presumably because of improved water infiltration and salt and Na leaching. The test site was in an area commonly known as "salt spots" by practical farmers. Yield response from the high rate of acid application (5 Mg ha^{-1}) was somewhat lower than the low rate of acid application, presumably because of inadequate leaching of salts generated by the acid treatment. Note that this soil was highly saline (EC_e = 12 dS m^{-1}). A field study conducted in Israel (Oron and DeMalach, 1989) has shown that sulfuric acid applied between furrows at a rate of 4 Mg ha^{-1} has increased yields of cotton in slightly Na-affected soils (ESP of 7% in the top 60 cm) irrigated with sewage water having an EC of 1.8 to 1.9 dS m^{-1}.

There are many studies where improvements in nutrient availability were tested in nonsodic calcareous soils. Such subjects are beyond the scope of this chapter, and one may refer to a separate review article (e.g., Stromberg and Tisdale, 1979). These studies have shown that acid applications were effective in alleviating Fe, P, and Zn deficiency in various crops. The rate of acid or sulfur application to achieve the desired nutritional responses varies from 500 kg ha^{-1} to several Mg per ha, depending on the $CaCO_3$ contents of the soil, the crops and the methods of application. The longevity of such treatments has not yet been determined adequately. If the acid band remains undisturbed, a study with a tree crop, pecans (*Carya illinoensis*), shows that the effect of subsurface acid bands can last at least for 9 years after application in supplying Zn to the trees

(Fenn et al., 1990). A similar treatment with sulfur was also reported to be effective in correcting chlorosis in citrus (McGeorge, 1939). The longevity factor has a significant impact on cost-effectiveness of acid or sulfur application as compared to conventional means of fertilization or foliar spray in providing micronutrients.

B. Reclamation of Highly Sodic Alkaline Soils

Alkaline soils containing high levels of exchangeable Na (e.g., ESP of 35 to 100%) are distributed throughout the arid and semiarid regions of the world. Some of these soils also occur in coal mining areas affected by disposal of oilfield brine. These soils present not only the common problem of low permeability but also high pH and, at times, high salinity and are often void of vegetation, structurally unstable, and highly erodible. In reclaiming these soils, the primary targets are to lower the exchangeable Na, to improve water infiltration and soil structural stability, and to lower soil pH. The quantities of chemical amendments required are usually larger, in theory, than those used for moderately sodic soils, and in many cases high costs of amendments make reclamation unattractive. However, if the soil is sandy, it can be readily reclaimed.

1. Reclamation of Highly Sodic Sandy Alkaline Soils

Sandy soils, even when saturated with Na, have been reclaimed with the use of amendments with minor adjustments in crop selection. These soils have inherently large water conducting pores and low cation exchange capacities (CEC), the feature favorable for Na replacement and leaching. Highly sodic Fresno silt loam reclaimed in the Central Valley of California was saturated with Na, but the CEC ranged from 0.06 to 0.12 eq kg^{-1} (Overstreet et al., 1951). Likewise, the alkaline soils reclaimed in northwestern states are mostly silt loam in texture (Robbins, 1986). Prior to amendment application, the land to be reclaimed for crop production may require subsoiling, leveling, or grading so as to avoid ponding of water in low lying areas. The first crop during or after reclamation usually consists of forages and grains, most of which are salt-tolerant, easy to grow, and produce substantial biomass.

Amendment Requirements. The quantities of acid and acidulants required for Na replacement in sodic sandy soils are lowered by the low CEC. If the CEC of the soil is as low as 0.10 eq kg^{-1}, as is the case with Fresno silt loam, the quantity of sulfuric acid required to lower ESP from 100 to 15% in the top 30 cm is, according to Eq. (13), 12 Mg ha^{-1}, or 6 Mg ha^{-1} for 15 cm of soil thickness. These rates are not greatly different from the quantities required for reclamation of moderately sodic soils with high CEC (Table 5).

The quantities of acids or acidulants required to lower the pH of alkaline soils to 8.3 (an equilibrium pH of calcareous soils) are usually lower than those needed for Na replacement, unless the soils contain a large amount of alkali

generating minerals, such as soda ($Na_2CO_3 \cdot 10H_2O$) and trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$).

Improving Water Infiltration. There has been concern that the quantities of amendment required to replace Na from the surface soil may not be adequate to provide water infiltration necessary for leaching in Na-saturated soils. This concern is certainly warranted with elemental or even colloidal sulfur, as the oxidation reaction is too slow to be effective for initial leaching. In the case of H_2SO_4, soil column studies have shown that acid broadcast applications at a rate of 10 to 15 Mg ha^{-1} are usually sufficient to attain water infiltration necessary for initial leaching, even in clay loam soils which have a CEC as high as 0.40 eq kg^{-1} (Table 8). In the sandy textured Fresno soil series, satisfactory water infiltration was attained from sulfuric acid applied at 3 Mg ha^{-1} (Overstreet et al., 1951). When acid application rates approach 10 to 20 Mg ha^{-1}, infiltration rates may actually slow for the reasons stated earlier. Gypsum applications were not nearly as effective as sulfuric acid applications in improving water infiltration in highly sodic soils (Table 8), presumably because of limited solubility. Gypsum powder applications in excess of about 30 Mg ha^{-1} actually reduced water infiltration (Table 8) as a result of soil pore plugging

Table 8 Effects of Sulfuric Acid and Gypsum Application on Water Penetration into Dry Sodic Calcareous or Alkaline Soils

Soil types and properties						
Acid (Mg ha^{-1})	0	1.0	5.0	10.0	15.0	20.0
Gypsum (Mg ha^{-1})	0	1.75	8.75	17.5	26.2	35.0
Pima clay loam (CEC = 0.3 eq kg^{-1}, ESP = 25%, ECe = 17 dS m^{-1})						
Penetration (cm/5 hrs)						
Acid	13	16	19	21	17	—
Gypsum	13	17	18	18	17	—
Fresno silt loam (CEC = 0.09–0.11 eq kg^{-1}, ESP = 80–100%, EC_e = 8–13 dS m^{-1})						
Penetration (cm/5 weeks)						
Acid	31	40	52	—	—	—
Gypsum	31	—	4	—	—	—
Stewart silt loam (CEC = 0.26 eq kg^{-1}, ESP = 100%, EC_e = 56 dS m^{-1})						
Penetration (cm/5 hrs)						
Acid	10	12	33	57	80	62
Gypsum	10	11	19	24	29	26
Playa clay loam (CEC = 0.51 eq kg^{-1}, ESP = 100%, EC_e = 40 dS m^{-1})						
Penetration (cm/5 hrs)						
Acid	3	7	16	25	26	26
Gypsum	3	6	7	11	12	13

Source: Yahia et al., 1975; Overstreet et al., 1951.

with fine undissolved gypsum particles (Keren et al., 1980). In a field trial conducted on sodic alkaline sandy clay loam (ESP = 93–95% and pH of 10) in India, however, sulfuric acid applied at 7.5 and 13 Mg ha^{-1} did not yield significantly higher rates of water infiltration than gypsum or aluminum sulfate applied at chemically equivalent rates (Chand et al., 1977). In this experiment, sulfuric acid was apparently spread on a thin layer of standing water. If sulfuric acid was broadcast on dry soils as were other amendments, the results could have been different.

It should be kept in mind that these data were obtained with air-dry soils (except for the acid treatment in the field test in India), which are well-aggregated owing to the presence of high levels of salts. Once these soils, especially clay loam, are wet with low salt water, water infiltration is usually severely reduced because of aggregate slaking and destruction. Data related to the effect of chemical amendments on wet sodic soils under high water tables are currently scarce.

Soil and Crop Response. In the field trial on Na-saturated silt loam in California (Overstreet et al., 1951), acid and gypsum broadcast treatments lowered ESP from an initial value of 100 to 22 and 42%, and soluble Na concentrations from about 300 to 130 meq L^{-1} in the soil extract (Table 9). In addition, the pH measured in 1:5 extract was reduced from 9 to 8.6 and 7.7 with the gypsum and the acid treatments, respectively. The treatment with an equivalent rate of an unspecified form of elemental S decreased neither ESP nor soluble Na concentrations. These soil samples were collected from a soil depth of 0 to 30 cm at one monitoring location per plot about 8 months after the treatments. Because of the limited number of soil samples analyzed, these data should be considered merely an indication. Nonetheless, the observed reduction in ESP seems to have fallen well below the target. Application of sulfuric acid at 12.5 Mg ha^{-1} or gypsum at 22 Mg ha^{-1} should, according to Eq. (13), have lowered ESP to 15% instead of the observed range of 22 to 42%. In the field test in India (Chand et al., 1977), the application of sulfuric acid, gypsum, and aluminum sulfate reduced the ESP of the top 15 cm soil below the target level of 15%. The pH of the soil was reduced to below 8.6 at the high rate of application and below 9.0 at the low rate of application, both in acid- and in gypsum-treated plots. The high rates of application were 13 Mg ha^{-1} of sulfuric acid and 22 Mg ha^{-1} of gypsum, and the low rate were equal to half of the high rates.

In the field experiment with Fresno silt loam (Overstreet et al., 1951), yields of mixed pasture consisting of seven species of moderately to high salt tolerant grass species and clover (*Trifolium hybridum*) have shown consistently superior performance of the acid treatment over the gypsum treatment in all cuttings (Table 9). A good stand of clovers was reportedly obtained only in acid-treated plots. The sulfur treatment did not perform well, and this was thought to be a

Table 9 Effects of Three Amendments Applied to Na-Saturated Fresno Silt Loam on Properties of Top 30 cm Soil and Forage Crop Yields

Amendments	Control	Elem S	$CaSO_4 \cdot 2H_2O$	H_2SO_4
Rate (Mg ha^{-1})	0	4.1	22	12.5
Soil properties				
CEC, initial (meq kg^{-1})	118	111	93	86
EC_e, initial (dS m^{-1})	14	8.0	15.0	7.0
ESP, initial (%)	89	77	97	101
After 8 months	65	76	22	42
Na, initial (meq L^{-1})	254	168	304	154
After 8 months	265	173	133	132
pH (1.5) initial	9.5	9.6	9.0	9.1
After 8 months	9.6	9.4	8.6	7.7
Forage production		Mg ha^{-1}		
1st cut 9 months	3.23	3.76	5.28	7.63
2nd cut 1 year	2.33	2.57	3.38	4.33
3rd cut 1.5 years	1.83	1.69	2.60	4.86
Total 1.5 years	7.39	8.03	11.40	16.83

Source: Overstreet et al., 1951.

result of poor oxidation under the high-pH and high-salt environment. The superior performance of sulfuric acid treatment in this test remains unexplained, especially in light of comparable performance of gypsum in lowering ESP as well as soluble Na. Among the soil properties measured, the soil pH seems to be the only parameter that has changed differently between the two treatments. In a separate greenhouse experiment conducted on Na-saturated Playa silt loam with a pH of 10.3, acid treatments at a rate of 10 Mg ha^{-1} lowered the pH to 8.3 and produced respectable alfalfa (*Medicago sativa*) yields, while gypsum applications at the equivalent rate (17.5 Mg ha^{-1}) resulted in little production (Stroehlein et al., 1978). Soil analyses for P and Fe revealed no deficiency. It is probable that the superior performance of acid treatments in both of these experiments may be related to alleviating hydroxide toxicity (Thorup, 1969). In the field experiment conducted in India (Chand et al., 1977), sulfuric acid, gypsum, and aluminum sulfate treatments have provided about equal soil pH and yields of barley (*Hordeum vulgare*). In rice (*Oriza sativa*), however, the sulfuric acid treatment provided significantly greater yields and Zn concentrations in tissue. Rice yields as well as Zn concentrations from aluminum sulfate treatment were, however, significantly lower than those of the gypsum treatment, presumably owing to Al induced Zn deficiency.

2. Reclamation of Highly Sodic Alkaline Soils Involving Reclamation Crops

When soil texture changes from silt loam to clay loam, the cation exchange capacity (CEC) usually doubles or triples. Accordingly, the quantities of amendments required for the same level of ESP will, in theory, double or triple, leading to acid requirements in a range of 30 Mg ha^{-1} to as high as 100 Mg ha^{-1}. These rates are beyond the current investment strategy of most farmers. A classic strategy to deal with this situation is the use of reclamation crops.

Amendment Requirements. There is currently no accepted procedure to determine the amendment requirements for reclamation involving reclamation crops. However, the quantities can be determined appropriately based on the need to provide water infiltration sufficient to obtain initial leaching. The experimental data reviewed earlier indicate that the application rates of 10 to 15 Mg ha^{-1} in H_2SO_4 equivalent should be adequate to provide initial water intake, even in clay loam soils having a CEC as high as 0.4 eq kg^{-1}, provided that the soil is not wet. Application rates can be reduced in sandy soils or when saline water is used for irrigation. Such a rate of amendment application, however, may not lower ESP beyond the top 10 to 30 cm, depending primarily on the CEC. Removal of the exchangeable Na in deeper depths must then rely on cropping effects. These application rates, if sulfuric acid is to be used, should also be sufficient to lower soil pH to a satisfactory level in most alkaline soils.

Reclamation Crop Selection. Selection of reclamation crops has been primarily based on practicality and adaptability; it extends from rice and forage crops to trees (e.g., Gupta and Abrol, 1990). In essence, the underlying idea has been to grow whatever may grow in highly saline and/or alkaline soils with hope of soil improvements and some economic return. The presence of organic matter in reclamation of sodic alkaline soils has been viewed as having positive effects on soil structure, although some studies (e.g., Gupta et al., 1984) do not necessarily support this idea in sodic soils. A recent lysimeter study with Freedom silt loam (ESP = 68%, ECe = 2.4 dS m^{-1}) is among the few that have provided a rational basis for selecting crops for reclamation of Na-affected calcareous soils. The study examined the role of reclamation crops in improving water infiltration and removing exchangeable Na. Results indicate that the crops that produce a large root mass and CO_2, such as sorghum and sudan (*Sorghum sudanese*), provided the largest removal of exchangeable Na and improvements in water infiltration as compared to crops of lower root mass such as cotton (*Gosypium hirsutum*). The lysimeter study has also shown that the exchangeable Na removed by live plants was greater in extent and has reached deeper into the soil profile than the results attained by the incorporation of applicable crop residues. The field study conducted in India (Chand et al., 1977) also indicates that surface incorporation of organic matter, such as manure, had a lim-

ited value in reducing ESP, even though the decomposition of organic matter generates CO_2. A study conducted on nonsodic soils shows appreciable effects of crops on water infiltration (e.g., Ali and Swartzendruber, 1994). These studies seem to indicate that both CO_2 generation rates and root mass would be important criteria for selecting reclamation crops.

One can certainly wonder how any crops can be grown adequately without chemical amendments in the soil with ESP as high as 68%, because of the well-known difficulties with water infiltration. In the lysimeter experiment, the soil used (Freedom silt loam) was apparently sandy enough to permit adequate water infiltration. If not, an application of acids should provide the necessary initial water infiltration. An alternative may be to use saline water for leaching while maintaining soil permeability. In such cases, crops of higher salt tolerance than ordinary crops may be required. There are many plant species that have higher salt tolerance and are capable of producing large biomass, as reviewed elsewhere (Miyamoto et al., 1994). Improvements in water infiltration per se, however, may not lower soil pH to a desirable level for crop growth in sodic alkaline soils, unless acids or acidulants are used as amendments. Selection of reclamation crops based on their adaptability to high pH conditions then becomes a consideration (Kumar Ashok and Abrol, 1986).

Soil and Crop Response. There are many reports that claim that highly sodic alkaline soils were reclaimed by the use of reclamation crops. In many instances, such claims seem to refer to the success of establishing reclamation crops, because of their adaptability to saline sodic or alkaline conditions, but not necessarily improving the soil for subsequent cropping with a higher economic value. The lysimeter experiment with Freedom silt loam (Robbins, 1986) is among the few that actually demonstrated the major effects of reclamation crops on reducing ESP. The ESP of the soil was, for example, reduced from 68 to 30% to a depth of 0.7 m through cropping with sorghum or sudan in a matter of one season, which was more than the ESP reduction caused by the gypsum treatment without cropping. The effect of the gypsum treatment in removing the exchangeable Na was confined to the top 0.3 m. There are also other reports documenting favorable changes in soil properties following vegetation establishment in alkaline soils (e.g., Singh et al., 1990), although these results are not as spectacular as the results of the lysimeter experiment with Freedom silt loam.

It is, however, necessary to point out that the lysimeter study with Freedom silt loam is in apparent contradiction with the field study conducted on Fresno silt loam, where the reduction in ESP was minimal with cropping alone (Overstreet et al., 1951). Poor growth of crops in the field experiment and general slowness of reclamation with cropping may partly account for the apparent discrepancy. It is also possible that the difference in the extent of drainage between the two experiments may account for the apparent discrepancy. The lysimeter

experiment used a large quantity of water and deliberate leaching, while the field experiment with Fresno silt loam did not. It seems that the effective removal of exchangeable Na cannot be achieved without adequate leaching, regardless of how the Ca was solubilized, either through CO_2 respiration or $CaCO_3$ dissolution with acids.

The complete picture of reclamation involving reclamation crops with or without chemical amendments cannot be ascertained without a comprehensive reclamation model. At the moment, it seems that the principal role of acids and acidulants (or other chemical amendments) in reclamation of highly sodic alkaline soils is to facilitate crop establishment by improving surface soil conditions (including soil pH) and to provide water intake necessary for leaching, until cropping itself can carry out such functions.

3. Use of Acids on Revegetation of Highly Sodic Soils

Highly sodic soils are found more frequently under dryland conditions than in irrigated lands in most parts of arid and semiarid regions. Sodic lands are also being formed through saline seeps, strip mining activities (Sandoval and Gould, 1978), and as a result of disposal of oil field brine or drilling mud (McFarland, et al., 1987). Reclamation of these sodic lands is considered important, not only for soil and habitat conservation, but also for minimizing water quality degradation caused by suspended soil particles and salts. These concerns prompted the passage of various restoration regulations. Reclamation of sodic mine spoils is an example of regulatory measures placed on strip mining areas in the western states. A similar measure, though less stringent, is beginning to be enforced in the restoration of rangelands affected by disposal of oifield brine.

In the case of strip mining, a standard measure for reclamation is to top-dress salt or sodium affected spoils with native topsoil. This measure is costly but effective, provided that the topsoil is available in sufficient quantity. Otherwise, it is necessary to use measures to improve the properties of sodium-affected spoils or bring in exotic species that can adapt to the saline sodic soil conditions. In the case of revegetation of lands contaminated by oil field brine, top-dressing is usually not mandatory. Chemical amendments (especially the use of gypsum) have been thought to be an option in these cases (Doering and Willis, 1975), yet its uses are essentially at an experimental stage. In a preliminary pot experiment (Scholl and Miyamoto, 1984) involving coal mine spoils derived from Na-affected sandstone (initial ESP of 21% with EC_e of 6.7 dS m^{-1}), broadcast applications of sulfuric acid at a rate of 2.5 and 5.0 Mg ha^{-1} reduced ESP and improved water infiltration, availability of P, and top dry weights of two salt tolerant range plants (Table 10). In Na-affected spoils derived from shale (ESP = 38%, EC_e = 5.2 dS m^{-1}), however, acid applications at a rate of 5.0 Mg ha^{-1} caused a significant reduction in seedling emergence, presumably owing to excessive acidification to lower the pH of the surface soil

Table 10 Some Chemical and Physical Properties of Coal Mine Spoils and Performance of Two Range Grass Species as Affected by Sulfuric Acid and Gypsum Treatments of Potted Soils

Amend type	Control	Sulfuric acid		Gypsum		Sand mulch
Rate (Mg ha^{-1})	0	2.5	5.0	5.0	5.0 + P[a]	1.25 cm
Sandstone spoil (initial ESP = 21%, EC_e = 6.9 dS m^{-1}, pH = 8.0)						
ESP (%)	19	7	4	6	6	—
Water penetrat. (cm/h)	3	8	11	5	5	—
EC_e(dS m^{-1})	6.7	7.2	8.1	7.4	7.4	—
pH (0–7.0 cm)	7.9	7.7	7.4	7.9	7.9	—
(0–2.5 cm)	—	—	6.9	—	—	—
$NaHCO_3$ ext P (mg kg^{-1})	7	14	16	7	62	—
Emergence (%)						
Sacaton	71	74	76	71	57	—
Saltbush	13	18	21	14	12	—
Shale spoil (initial ESP = 38%, EC_e = 5.5 dS m^{-1}, pH = 8.3)						
ESP (%)	35	14	7	23	23	15
Water penetrat. (cm/hr)	1	4	6	2	2	—
EC_e (dS m^{-1})	5.2	6.5	7.7	5.7	5.7	4.2
pH (0–7.0 cm)	8.2	7.3	6.9	8.0	8.0	8.2
(0–2.5 cm)	—	—	4.8	—	—	—
$NaHCO_3$ ext. P	2	4	5	2	72	1
Emergence (%)						
Sacaton	56	71	7	57	57	75
Saltbrush	9	15	4	22	22	19
Top dry wt. (g/pot)						
Sacaton	1.3	1.6	0.2	1.0	3.5	1.4
Saltbush	1.2	2.5	1.9	1.7	3.3	2.0

[a]Applied as CaH_2PO_4 at 200 kg ha^{-1}.
Source: Scholl and Miyamoto, 1984.

to 4.8 (Table 10). In both cases, a gypsum application at 5 Mg ha^{-1} resulted in insignificant increases in water infiltration and crop response. However, the gypsum application combined with phosphorus application increased plant growth. This experiment was conducted in a 7 cm deep pot with water application insufficient to cause any drainage. In a separate greenhouse study, many of the range plant species common to the Southwestern US were found to respond to P and Fe applications in calcareous soils (Ryan et al., 1975c).

These exploratory studies seem to indicate that the effects of acid application to mine spoils consisting of Na-affected sandstone are similar to those observed in irrigated calcareous soils. In spoils developed from shale, however, these studies have shown a possibility of excessive acidification and poor release and/or subsequent precipitation of P. Low pH can affect seed germination (Ryan et al., 1975a). An additional concern is poor leaching of dissolved salts in dryland situations because of limited precipitation. The dissolved salt concentrations usually increase with acid application, whereas gypsum applications usually result in only modest increases in salinity owing to its limited solubility. The limited solubility of gypsum, however, usually means slow effects, especially under limited rainfall. In order to dissolve 5 Mg ha^{-1} of gypsum, at least 20 cm of water is needed, which is higher than the annual precipitation in most arid areas. The dissolution of gypsum is further curtailed by the presence of high levels of SO_4^{-2} in coal mine spoils.

Band application of sulfuric acid (or gypsum) may be an option to enhance rainfall utilization for leaching. In a soil box study (Yahia et al., 1975), acid bands 10 cm wide were placed every 50 cm at an acid application rate of 2 Mg ha^{-1} on Na-saturated Stewart silt loam and Playa clay loam, followed by leaching using 6.5 cm of water. (The acid application rate on the basis of the treated area amounted to 10 Mg ha^{-1}.) Increased water infiltration in the acid band caused the ponded water to infiltrate predominantly through the band. Consequently, soluble salts were leached in a radial direction from the band, resulting in lower salinity below the acid bands than under the broadcast application (Table 11).

Table 11 Effects of Banded and Broadcast Applications of Sulfuric Acid at 2 Mg ha^{-1} on Initial Salt Leaching and Subsequent Dry Matter Production of Two Range Plant Species in Na-Saturated Stewart Silt Loam with the Initial EC_e of 42 dS m^{-1}.

Application methods	Banded		Broadcast	
Initial soil salinity after 6.5 cm water application				
Soil depth cm	EC_e dS m^{-1}		EC_e dS m^{-1}	
1	8		30	
10	6		26	
20	32		52	
Dry matter production after 4 months				
	Banded kg ha^{-1}		Broadcast kg ha^{-1}	
Irrigation cm	Bermuda	Sacaton	Bermuda	Sacaton
5.5	9.1	8.3	1.7	0.0
11.0	24.0	16.0	5.2	4.8

Source: Unpublished data, author's laboratory.

The acid treated soils were left for one month, and seeded with alkali sacaton (*Sporobolus airoides*) and common bermuda (*Cynodon dactylon*), using 5 and 10 cm of distilled water. Under the broadcast treatment, 30% of the seed germinated at 5 cm of water application and 70% at 10 cm of water application (unpublished report). Under the banded treatment, germination in the acid band exceeded 70%, but it declined to zero 11 cm away from the edge of the acid band. The top dry weights measured after 4 months indicate superior performance of the banded treatment over the broadcast treatment (Table 11).

No published report is currently available concerning the effect of sulfuric acid on revegetation of sodic soils on a field scale. However, judging from the exploratory work, acid treatment may help establish vegetation when combined with various water-catchment measures employed in range management. Obviously, additional research is needed to establish effective uses of acids and acidulants in such applications.

VI. SUMMARY

The use of acidulants on alkali soils began in the 1930s, mostly as a substitute for gypsum. Subsequent studies have shown that acids and acidulants have the unique ability to improve structural stability of sodic soils, to remove carbonates from irrigation water and calcareous soils, to improve availability of micronutrients and phosphorus, and to lower high pH of irrigation water and alkaline soils. In the category of water conditioning, sulfuric acid and its blends with nitrogen fertilizers are used primarily to reduce Ca precipitation and to maintain infiltration of low salt or ammoniated water. Polysulfides have been used to lower sodicity of surface soils and for improving water penetration. The cost-effectiveness of acid uses for water conditioning can be improved through blending with nitrogen fertilizers and improved guidelines for uses on diverse soil and water conditions. In the category of soil treatments, sulfuric acid and sulfur compounds are used primarily to improve water infiltration, availability of certain nutrient elements, and soil reactions in sodic calcareous or sodic alkaline soils. Sulfuric acid seems to hold a definite advantage over gypsum in reclamation of highly sodic alkaline soils, or calcareous sodic soils with micronutrient or phosphorus deficiency, whereas elemental S applications seem to suffer from slow and often inconsistent oxidation. In spite of these potential advantages of acids, handling difficulties present a challenge. The use of acids and acidulants for soil treatments can be made effective through improved understanding of pH effects on soil structural stability, nutrient availability, hydroxide toxicity, and the role of reclamation crops in reclaiming highly sodic soils. With increasing costs of crop production, and increasing regulations and costs of handling acids and acidulants, there is a continuing need to improve application strategies and methods. Acids and acidulants should not be regarded simply as substitutes for gypsum.

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REFERENCES

Abu-Sharar, T. M., Bingham, F. T., and Rhoades, J. D. (1987). Reduction in hydraulic conductivity in relation to clay dispersion and disaggregation. *Soil Sci. Soc. Am. J. 57*:342–346.

Achorn, F. P. (1984). Acid fertilizers. *Solution 3*:33–39.

Alawi, B. J. (1977). Effect of irrigation water quality, sulfuric acid and gypsum on plant growth and on some physical and chemical properties of Pima soil. Ph.D. diss., Univ. of Arizona.

Ali, A. M. (1989). Reactions of urea phosphate in calcareous and alkali soils:ammonia volatilization and effects on soil sodium and salinity. Ph.D diss. Univ. of Arizona.

Ali, A. S. I., and Swartzendruber, D. (1994). An infiltration equation to assess cropping effects on soil water infiltration. *Soil Sci. Soc. Am. J. 58*:1218–1223.

Baumhardt, R. L., Wendt, C. W., and Moore, J. (1992). Infiltration in response to water quality, tillage and gypsum. *Soil Sci. Soc. Am. J. 56*:261–266.

Beaton, J. D., and Fox, R. L. (1971). Production, marketing, and use of sulfur products. *Fertilizer Technology and Use* (R. A. Olson, T. J. Army, J. J. Hanway, and V. J. Kilmer, eds.). Soil Science Society of America, Madison, Wisconsin.

Bower, C. A., and Fireman, M. (1957). Saline and alkali soils. In *Year Book of Agriculture 1957*. (A. Stettrud, ed) USDA, Washington, D.C. pp. 282–290.

Burns, G. R. (1967). Oxidation of sulphur in soils. Sulphur Institute of Technological Bulletin 13. Washington, D.C.

Chand, M., Abrol, I. P., and Bhumbla, D. R. (1977). A comparison of the effect of eight amendments on soil properties and crop growth in a highly sodic soil. *Indian J. Agric. Sci. 47*:348–354.

Doering, E. J., and Willis, W. O. (1975). Chemical reclamation for sodic strip-mine spoils. USDA ARS ARS-NC-20.

Dudal, R., and Purnell, M. F. (1986). Land resources: salt-affected soils. *Recl. Reveg. Res. 5*:1–9.

Eaton, F. M. (1950). Significance of carbonates in irrigation water. *Soil Sci. 69*:123–133.

Fenn, L. B., and Miyamoto, S. (1981). Ammonia loss and associated reactions of urea in calcareous soils. *Soil Sci. Soc. Am. J. 45*:537–540.

Fenn, L. B., Malstrom, H. L., Riley, T., and Horst, G. L. (1990). Acidification of calcareous soils improves zinc absorption of pecan trees. *J. Am. Soc. Hort. Sci. 115*:741–744.

Gilbert, R. G., Nakayama, S., and Bucks, D. A. (1979). Trickle irrigation: prevention of clogging. *Trans. ASAE 22*(3):514–519.

Gumaa, G. S., Prather, R. J., and Miyamoto, S. (1976). Effect of sulfuric acid on sodium-hazard of irrigation water. *Plant Soil 44*:715–721.

Gupta, R. K., and Abrol, I. P. (1990). Salt-affected soils: their reclamation and management for crop production. *Ach. Soil Sci. 11*:223–288.

Gupta, R. K., Bhumbla, D. K., and Abrol, I. P. (1984). Effect of sodicity, pH, organic matter and calcium carbonate on the dispersion behavior of soils. *Soil Sci. 137*:245–251.

Haynes, J. D. (1928). Studies with sulfur for improving permeability of alkali soil. *Soil Sci. 25*:443–446.

Helmers, S. G., and Miyamoto, S. (1990). Mechanical and physical practices for reducing salinity in pecan orchards. *Proc. 3rd Nat. Irrig. Sympos.*, ASAE, St. Joseph, Michigan, pp. 374–377.

Hilgard, E. W. (1889). The rise of the alkali in the San Joaquin Valley. *Univ. Calif. Exp. Sta. Bull. 83*.

Kelley, W. A., and Brown, S. M. (1934). Principles governing the reclamation of alkali soils. *Hilgardia 8*:149–177.

Keren, R., and O'Connor, G. A. (1982). Gypsum dissolution and sodic soil reclamation as affected by water flow velocity. *Soil Sci. Soc. Am. J. 46*:726–732.

Keren, R., Kreite, J. F., and Shainberg, I. (1980). Influence of size of gypsum particles on the hydraulic conductivity of soils. *Soil Sci. 130*:113–117.

Khorsandi, F. (1994). Phosphorus fractions in two calcareous soils as affected by sulfuric acid application. *J. Plant Nutri. 17*:1599–1609.

Kumar Ashok, and Abrol, I. P. (1986). Grasses in alkali soils. Bull. 2, Central Soil Salinity Research Institute, Karnal, India.

Leclercq, R., Bixby, D. W., and Fike, H. L. (1972)). Potential uses for sulphur dioxide. Tech. Bull. 19, Sulphur Institute, Washington, D.C.

Mathers, A. C. (1970). Effect of ferrous sulfate and sulfuric acid on grain sorghum yields. *Agron. J. 62*:555–556.

McCaskill, M. R., and Blair, G. J. (1987). Particle size and soil texture effects on elemental sulfur oxidation. *Agron J. 79*:1079–1083.

McFarland, M. L., Ueckert, D. N., and Hartmann, S. (1987). Revegetation of oil well reserve pits in west Texas. *J. Range Mgt. 28*:411–414.

McGeorge, W. T. (1939). Some problems connected with fertilization of alkali soils. *Calif. Citrogr. 24*:389.

McGeorge, W. T. M., and Green, R. A. (1935). Oxidation of sulphur in Arizona soils and its effect on soil properties. *Ariz. Agr. Exp. Sta. Tech. Bull. 59*:297–325.

McGeorge, W. T., Breazeale, E. L., and Abbott, J. L. (1956). Polysulfides as soil conditioners. Arizona Agr. Exp. Sta. Bull. 131, University of Arizona, Tucson.

McKee, A. G., and Co. (1969). Systems study for control of emissions by the primary nonferrous smelting industry. *U.S. Federal Clearing House*. P.B. 184. Washington, D.C.

Miyamoto, S., and Cruz, I. (1987). Spatial variability of soil salinity in furrow irrigated Torrifluvents. *Soil Sci. Soc. Am. J. 51*:1019–1025.

Miyamoto, S., and Enriquez, C. (1990). Comparative effects of chemical amendments on salt and Na leaching. *Irrig. Sci. 11*:83–92.

Miyamoto, S., and Ryan, J. (1976). Sulfuric acid for the treatment of ammoniated irrigation water II. Reducing Ca precipitation and sodium hazards. *Soil Sci. Soc. Am. J. 40*:305–309.

Miyamoto S., and Stroehlein, J. L. (1975). For improving water penetration into some Arizona soils—sulfuric acid. *Prog. Agr. 27*(2):13–16.

Miyamoto S., Ryan, J., and Bohn, H. L. (1973). Penetrability and hydraulic conductivity of dilute sulfuric acid solutions in selected Arizona soils. *Proc. Amer. Water Res. Assn. Arizona Section*, pp. 291–298.

Miyamoto, S., and Stroehlein J. L. (1986). Sulfuric acid effects on water infiltration and chemical properties of alkaline soils and water. *Trans. ASAE 29*:1288–1296.

Miyamoto, S., Ryan, J., and Stroehlein, J. L. (1975a). Potentially beneficial uses of sulfuric acid in southwestern agriculture. *J. Environ. Qual. 4*:431–437.

Miyamoto S., Prather, R. J., and Stroehlein, J. L. (1975b). Sulfuric acid for controlling calcite precipitation. *Soil Sci. 120*:264–271.

Miyamoto S., Prather, R. J., and Stroehlein, J. L. (1975c). Sulfuric acid and leaching requirements for reclaiming sodium-affected soils. *Plant Soil 43*:573–585.

Miyamoto, S., Stroehlein, J. L., and Ryan, J. (1975d). Sulfuric acid for the treatment of ammoniated irrigation water. I. Reducing ammonia volatilization. *Soil Sci. Soc. Am. J. 39*:544–548.

Miyamoto, S., Glenn, E. P., and Singh, N. T. (1994). Utilization of halophytic plants for fodder production with brackish water in subtropic deserts. In *Halophytes as a Resource for Livestock and for Rehabilitation of Degraded Lands* (V. R. Squires and A. T. Ayoub, Eds). pp. 43–75. New York: Kluwer Academic Publishing.

Mohammed, E. T. Y. (1972). The effect of various sulphur compounds on infiltration of selected soils. Ph.D. diss., University of California, Riverside.

Morril, L. G., and Dawson, J. E. (1967). Patterns observed for the oxidation of ammonium to nitrate by soil organisms. *Soil Sci. Soc. Am. Proc. 31*:757–760.

Moser, U. S., and Olson, R. V. (1953). Sulphur oxidation in four soils as influnced by soil moisture tension and sulphur bacteria. *Soil Sci. 76*:251–257.

Oron, G., and DeMalach, Y. (1989). Effect of dikes and sulfuric acid on cotton under effluent irrigation. *J. Irrig. Drainage Engr. 115*:463–473.

Oster, J. D., and Schroer, F. W. (1979). Infiltration as influenced by irrigation water quality. *Soil Sci. Soc. Am. J. 43*:444–447.

Overstreet, R, Martin, J. C., and King, H. M. (1951). Gypsum, sulfur and sulfuric acid for reclaiming an alkali soil of the Fresno series. *Hilgardia 21*:113–127.

Paulina, Y. W., Li. (1951). The oxidation of elemental sulfur in soils. M.S. thesis, University of Minnesota.

Phillips, A. B., and Scott, W. C. (1966). Preparation and properties of ammonia–sulfur solutions. *Agr. Ammonia News 16*(3):40–46.

Phillips, A. B., and Webb, J. R. (1971). Production, marketing, and use of phosphorus fertilizers. *Fertilizer Technology and Use* (R. A. Olson, T. J. Army, J. J. Hanway, and V. J. Kilmer, eds). Soil Science Society of America, Madison, Wisconsin.

Robbins, C. W. (1986). Sodic calcareous soil reclamation as affected by different amendments and crops. *Agron. J. 78*:916–920.

Roberts, S., and Koehler, F. E. (1965). Sulfur dioxide as a source of sulfur dioxide for wheat. *Soil Sci. Soc. Am. Proc. 29*:696–698.

Robinson, F. E., Cudney, D. W., and Jones, J. P. (1968). Evaluation of soil amendments in the Imperial Valley. *Calif. Agr.* Dec. issue: 10–11.

Ryan, J., Miyamoto, S., and Stroehlein, J. L. (1974). Solubility of manganese, iron and zinc as affected by application of sulfuric acid to calcareous soils. *Plant Soil 40*:421–427.

Ryan, J., Miyamoto, S., and Stroehlein, J. L. (1975a). Effect of acidity on germination of some grasses and alfalfa. *J. Range Mgt. 28*:154–155.

Ryan, J., Stroehlein, J. L., and Miyamoto, S. (1975b). Sulfuric acid applications to calcareous soils. Effects on growth and chlorophyll content of common bermudagrass. *Agron. J. 67*:633–637.

Ryan, J., Stroehlein, J. L., and Miyamoto, S. (1975c). Effect of surface-applied sulfuric acid on growth and nutrient availability of five grasses in calcareous soils. *J. Range. Mgt. 28*:411–414.

Sandoval, F. M., and Gould, W. L. (1978). Improvement of saline- and sodium-affected disturbed lands. In: *Reclamation of Drastically Disturbed Lands*. American Society Agronomy, Madison, Wisconsin, pp. 485–504.

Scholl, D. G., and Miyamoto, S. (1984). Response of alkali sacaton and fourwing salt bush to various amendments on coal mine spoils from northwestern New Mexico. II. Sodic Spoil. *Reclam Reveg. Res. 2*:243–252.

Scofield, C. S., and Headly, F. B. (1921). Quality of irrigation water in relation to land reclamation. *J. Agric. Res. 21*:265–278.

Shainberg, J., and Letey, J. (1984). Response of soils to sodic and saline conditions. *Hilgardia 52*(2):1–57.

Singh, G., Abrol, I. P., and Cheema, S. S. (1990). Effects of irrigation on *Prosopis juliflora* and soil properties of an alkali soil. *Inter: Tree Crop J. 6*:81–99.

Stroehlein, J. L., Miyamoto, S., and Ryan, J. (1978). Sulfuric acid for improving irrigation waters and reclaiming sodic soils. *Agri. Engr. and Soil Sci. Bull. 78*:5. University of Arizona, Tucson, AZ.

Stromberg, L. K., and Tisdale, S. L. (1979). Treating irrigated arid-land soils with acid-forming sulfur compounds. Tech Bull. 24. Sulphur Institute, Washington, D.C.

Suarez, D. L., Rhoades, J. D., Lavado, R., and Crieve, C. M. (1984). Effect of pH on saturated hydraulic conductivity and soil dispersion. *Soil Sci. Soc. Am. J. 48*:50–55.

Thorup, J. T. (1969). pH effect on root growth and water uptake by plant. *Agron J. 61*:225–227.

Tisdale, S. L. (1968). Sulphur as fertilizer. *New Fertilizer Materials* (Y. Araten, ed.). Centre International Engrais Chimiques. Noyes Development Corp., Rark Ridge, N.J.

Tisdale, S. L. (1970). The use of sulfur compounds in irrigated arid land agriculture. *Sulphur Inst. J. 6*(1):2–7.

Tobia, K., and Pollard, A. G. (1958). Effects of acidification of alkali and calcareous soils. *J. Sci. Food Agric. 9*:705–713.

U.S. Salinity Laboratory Staff (1954). Diagnosis and improvement of saline and alkali soils. USDA Handbook 60 (L. A. Richards, ed.).

Vodyanitskiy, Y. N., and Dokuchayev, V. V. (1985). Use of iron compounds for soil aggregation. *Poch vovedeniye 12*:49–54 (English translation).

Wallace, A., and Mueller R. T. (1978). Complete neutralization of a portion of calcareous soil as a means of preventing chlorosis. *Agron. J. 70*:888–890.

Weiss, F. T., Jungnickel, J. L., and Peters, E. D. (1953). Analysis of sulfuric acid and acid sludges from petroleum processes. *Anal. chem. 25*:277–283.

Wildman, W. E., Pecock, W. L., Wildman, A. M., Goble, G. G., Pehrson, J. E., and O'Connell, N. V. (1988). Soluble calcium compounds may aid low volume water application. *Calif. Agric.*, Nov–Dec. issue: 7–9.

Yahia, T. A., Miyamoto, S., and Stroehlein, J. L., (1975). Effect of surface-applied sulfuric acid on water penetration into dry calcareous and sodic soils. *Soil Sci. Soc. Am. Proc. 39*:1201–1204.